

INTERNAL FRICTION AND DYNAMIC YOUNG MODULUS OF A BITUMINOUS COAL

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INTRODUCTION

Elastic properties of coal provide three types of information. First, elastic constants such as Young modulus and Poisson ratio provide essential engineering-design parameters. These parameters enter calculations for load-deflection, thermo-elastic stress, buckling instability, and crack propagation. Second, elastic constants provide valuable material characterization. They reflect differences in thermal-mechanical history, in void and crack content, and in chemical composition. Third, elastic constants relate closely to interatomic arrangements and interatomic forces. From interatomic force constants ("spring constants"), one can specify the complete set of elastic constants (two for isotropic symmetry, nine for orthotropic symmetry). Because coal exhibits three macroscopic orthogonal mirror planes, it must exhibit orthotropic elastic symmetry. Recently, for isotropic solids, Ledbetter [1] described elastic constants and their interrelationships with other physical properties.

As described by Nowick and Berry [2], internal friction, or anelasticity, amounts to the imaginary part of either elastic stiffness or elastic compliance. Internal friction manifests itself in many ways: width of a resonance peak, amplitude decay of a stress wave, phase lag of strain behind stress, and area within an elastic-region stress-strain loop. Each of these manifestations provides a possible measurement method. As described below, we used resonance-peak width. In crystalline solids, internal friction usually arises from various relaxations: point defects, dislocations, grain boundaries, phonons, magnetoelastic couplings, and electron configurations. In amorphous polymers, the principal relaxation arises from the glass transition, attributed to large-scale rearrangements of the principal polymer chain. At lower temperatures, one observes secondary relaxations caused by side groups capable of independent hindered rotations. Adapted from Houwink and de Decker [3], Fig. 1 shows for four polymers the internal friction versus temperature, which we often call the mechanical-loss spectrum. Most polymers fit the general pattern suggested in Fig. 1.

Recently, Szwilski [4] described a method for determining the anisotropic elastic moduli of coal. He reported seven previous studies of coal's elastic constants. Besides these seven, at least six other experimental studies exist: Constantino and Trettennero [5] and Wert, Weller, and Völker [6-10].

Wert and Weller [6-10] used a torsional pendulum at frequencies near 1 Hz to measure between 10 and 450 K the temperature dependence of both the torsional modulus, G , and the internal friction, $\tan \delta = Q^{-1}$. These authors were first to report coal's internal-friction spectrum, which reveals mechanical-relaxation phenomena. See Fig. 2. Based on their experimental studies, Weller and Wert support a polymeric model for coal. In the above temperature range, these authors detected three peaks (denoted α , β , γ) and possible evidence for a low-temperature peak (δ) near 50 K. These peaks correspond closely to those observed in most polymers. Wert and Weller [7] ascribe the α -peak to massive motion of macromolecules, related probably to the

glass transition. They ascribe the β -peak to reorientation under stress of side units, perhaps associated with water. They ascribe the γ -peak to twisting or other reorientation of segments of a linear section of CH_2 units. They believe this peak decreases with coal's increasing carbon content (rank).

The present study relates closely to those of Wert and Weller [6-10]. The principal differences are three: (1) We used larger specimens by a factor of approximately 40 in volume. (2) We used higher frequencies: 45 kHz to their 1 Hz. (3) We studied a Young-modulus (extensional) deformation mode while they studied a torsional mode. Twisting induces no volume changes while uniaxial stress involves both shear and dilatation.

MATERIAL

We studied a high-volatile Eastern-Kentucky bituminous coal studied previously by Wert and Weller [7], who reported a composition of 81.8% carbon (wt. pct. daf). Specific gravity measured at 293 K by Archimedes's method was 1.316.

SPECIMENS

We prepared square-cross-section rod specimens, 0.48 cm by 2.43 cm, by sawing. The specimen reported on here lay in the coal's bedding plane and along the major cleat direction. We determined this orientation visually, based on easily discernible striae and longitudinal markings.

MEASUREMENTS

For measuring the Young modulus, E , and internal friction, Q^{-1} , we used a Marx-composite-oscillator method [11-14]. At $T = 293$ K, the composite-oscillator resonance frequency was 45 kHz. Our version of this apparatus operates between 20 and 100 kHz in the fundamental mode. Using overtones permits higher frequencies. Cooling to liquid-nitrogen temperature (76 K) was achieved with a probe-and-dewar arrangement described elsewhere [13]. To obtain the Young modulus, one uses the relationship

$$E = 4\rho f_0^2 l^2 \quad (1)$$

where ρ denotes mass density, f_0 specimen resonance frequency for the fundamental (half-wavelength) mode, and l specimen length. In a Young-modulus deformation mode, the rod cross-section is immaterial, if it is uniform along the specimen length. To obtain internal friction, one uses the relationship

$$Q^{-1} = (f_2 - f_1)/f_0 \quad (2)$$

where f_1 and f_2 denote the frequencies at the half-power points of the resonance peak and f_0 denotes resonance frequency. Thus, versus frequency, one measures strain amplitude detected as the voltage generated in a piezoelectric quartz gage crystal. We did not correct for coal's contraction during cooling. Cooling rates were 2 K/min. A sweep over the resonance-frequency range required 40 s. Measurements made at lower cooling rates should show less scatter.

Concerning measurement uncertainties, our limited experience with this material precludes a precise statement. We guess that E is accurate within a few percent and Q^{-1} within about 20 percent. Scatter in Fig. 3 indicates the imprecisions.

RESULTS

Figure 3 shows the principal results: E and Q^{-1} versus temperature between 293 and 76 K. We show E as a dimensionless ratio to the ambient-temperature value.

DISCUSSION

Our ambient-temperature value, $E = 6.4$ GPa, exceeds considerably the range for coal reported by Constantino and Trettenero [5], 3.0 to 4.5 GPa, measured perpendicular to the bedding plane. But it falls within the 2.1 to 9.5 GPa range reported by Szwilski [4] for the bedding plane. To minimize effects of microcracks, Szwilski applied a small confinement force, which would not affect the intrinsic elastic constant. Compared with polymers, this Young modulus is only slightly lower. For example, for four technical polymers, Athougies et al. [15] reported the dynamic Young modulus which showed a range of 7 to 9 GPa.

The extrapolated increase in E during cooling to zero temperature, $E(0)/E(293) \cong 1.7$, lies considerably below the torsional-modulus increase found by Wert and Weller [7], $G(0)/G(293) \cong 2.6$. For isotropic materials, E and G relate simply through the bulk modulus, B :

$$E = 9BG/(3B+G). \quad (3)$$

By differentiation

$$\frac{\Delta E}{E} = \frac{1}{(3B+G)} \left(G \frac{\Delta B}{B} + 3B \frac{\Delta G}{G} \right). \quad (4)$$

Taking the Poisson ratio to be $1/3$, then [1]

$$\frac{\Delta E}{E} = \frac{1}{9} \left(8 \frac{\Delta G}{G} + \frac{\Delta B}{B} \right). \quad (5)$$

Thus, the large $\Delta G/G$ relative to $\Delta E/E$ must arise from another source, not from a smaller $\Delta B/B$ change, which contributes approximately one-ninth. One can identify four possible sources: measurement frequency, strain amplitude, temperature-dependent relaxation strength, and material anisotropy. Without further study, we can not comment on these possibilities.

Usually, one can describe the $E(T)$ behavior by a relationship [16]

$$E(T) = E(0) - s/\exp(t/T) \quad (6)$$

where $E(0)$ denotes zero-temperature Young modulus, s an adjustable parameter related to zero-point vibrations, t the Einstein temperature, and T temperature. This relationship fits the $E(T)$ measurements only approximately because of the irregularities in $E(T)$ that arise from cooling through some relaxation mechanisms, principally the γ peak. From a least-squares fit to the $E(T)$ results shown in Fig. 3, we obtain $t = 345$ K, a rough estimate of coal's effective Einstein temperature. In a preliminary study, Merrick [17] modeled coal's specific heat with an Einstein model. He made the usual Einstein-model interpretation: "the characteristic temperatures ... reflect the average properties of the bonds." For the temperature range 0-800°C, Merrick obtained $t = 1200$ K. A second approach used a two-Einstein-temperature model with $t_1 = 380$ K and $t_2 = 1800$ K. This model recognizes anisotropic binding forces: strong forces within layers and weaker forces between layers. It gives a lower $C_p(T)$ curvature and better agreement with measurement. We compare these

results with graphite where Komatsu [18] used a lattice-vibration model and the C_{44} elastic constant to predict that $t_1 = 135$ K and $t_2 = 1860$ K. We take this latter characteristic temperature as the upper bound of any "lattice" vibrations representing binding forces in coal. A better upper bound may arise from the $t = 1680$ K Einstein temperature of diamond [1], where the carbon-carbon tetrahedral-covalent bond strength exceeds that of any other known material.

We turn now to internal friction. Figure 3 shows a broad peak centered near 240 K, which we interpret as the Wert-Weller γ peak detected at 130 K. From eq. (3.5-5) in Nowick and Berry

$$Q = k \ln (\omega_2/\omega_1) (T_{p1}^{-1} - T_{p2}^{-1})^{-1} \quad (7)$$

where k denotes Boltzmann's constant, Q denotes activation energy, ω denotes angular frequency, and T_p denotes peak temperature, we obtain $Q = 0.26$ eV compared with 0.18 eV obtained by Wert and Weller [10].

The upturn in Fig. 3 just above 76 K signifies a strong low-temperature (δ) peak only suggested in some of the Wert-Weller studies. This peak requires further study by cooling to lower temperatures. This δ peak may appear stronger in our study because our higher measurement frequency (by a factor of $5 \cdot 10^5$) approaches more closely the δ -peak resonance frequency. From eq. (3.5-4) in Nowick and Berry

$$T_p = \frac{-Q}{k} \frac{1}{\ln \omega t_0} \quad (8)$$

where $t_0 = \nu_0^{-1}$ denotes a fundamental relaxation time and ν_0 a fundamental frequency related to a mechanical-relaxation mechanism. Thus, a lower T_p corresponds to either lower Q or lower ν_0 . Lower T_p usually corresponds to a smaller vibrating unit.

CONCLUDING REMARKS

Given that coal is a polymer, then the enormous body of pre-existing polymer physics should transfer to coal. This physics includes measurement methods, mechanical models (Kelvin, Maxwell, etc.), molecular interpretations, structure geometry, viscoelasticity theory, and anisotropic phenomena. Many books summarize the state of polymer physics; several relate especially to dynamical-mechanical properties: Alfrey [19], Tobolsky [20], Ferry [21], Heijboer [22], McCrum, Read, and Williams [23], Christensen [24], Ward [25], Baer and Radcliffe [26], Nielsen [27], Read and Bean [28], and Murayama [29].

From the materials-science viewpoint, the most important relationships are those between structure and macroscopic properties. For polymers, Murayama [29] summarized the dynamical-mechanical studies:

The investigation of the dynamic modulus and internal friction over a wide range of temperatures and frequencies has proven to be very useful in studying the structure of high polymers and the variations of properties in relation to end-use performance. These dynamic parameters have been used to determine the glass transition region, relaxation spectra, degree of crystallinity, molecular orientation, crosslinking, phase separation, structural or morphological changes resulting from processing, and chemical composition in polyblends, graft polymers, and copolymers.

Thus, one expects similar possible results in applying dynamical-mechanical methods to coal.

Our preliminary measurements show that, by dynamic methods, one can measure coal's elastic constants and mechanical-relaxation spectrum in a Young-modulus mode at kilohertz frequencies.

Boyer [30] pointed out that in studying the relaxation spectra of polymers one can focus on five different aspects: (1) experimental methods; (2) individual spectra as a characterization; (3) spectra features common to many materials; (4) correlation of loss peaks with other physical and mechanical properties; (5) molecular mechanisms of loss peaks. The second aspect includes effects of thermal history, crystallinity, measurement frequency, external force field, molecular orientation, and other variables.

Further studies at NBS could include eight principal efforts: (1) refine our preliminary measurements and extend them to both lower and higher temperatures; (2) determine the complete nine-component elastic-constant tensor; (3) attempt to relate the mechanical-relaxation peaks to mechanisms; (4) determine by measurement the changes of these peaks produced by variables such as moisture, heating, aging; (5) possibly relate microstructure to physical properties; (6) model the macroscopic elastic constants in terms of those of constituents; (7) determine complete damping tensor; (8) focus especially on the low-temperature δ -peak, which appears larger in our measurements than in previous ones.

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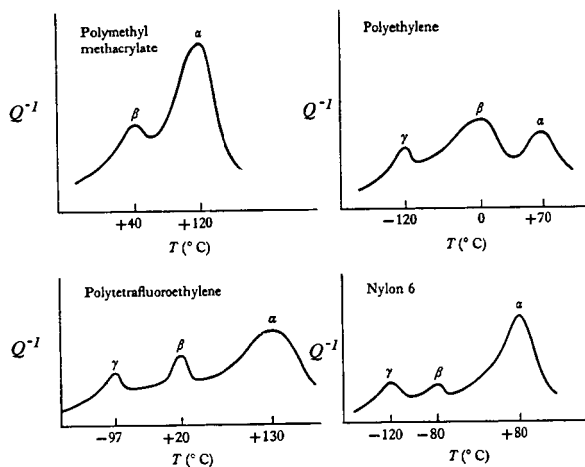


Fig. 1. Dynamic loss modulus versus temperature for four polymers; from Houwink and de Decker [3].

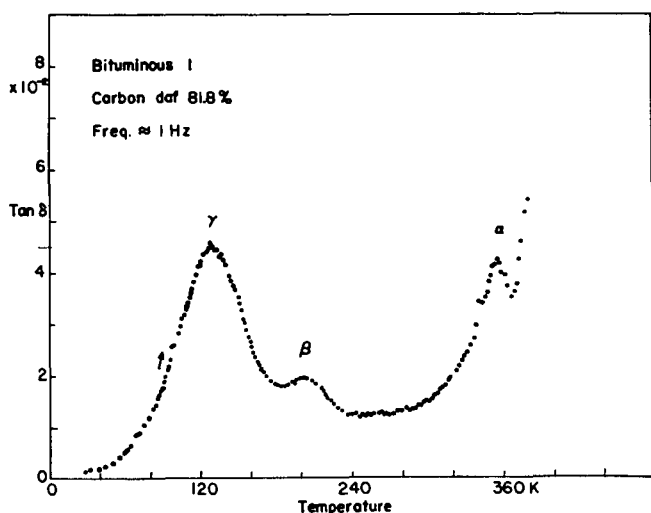


Fig. 2. Internal-friction spectrum of a bituminous coal; from Wert and Weller [7].

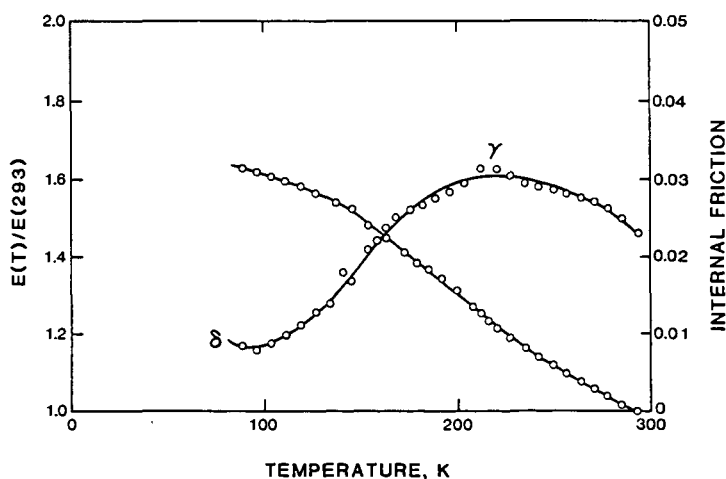


Fig. 3. Dynamic Young modulus and internal friction versus temperature measured near 50 kHz. A strong mechanical relaxation (γ) occurs near 240 K. A strong low-temperature peak (δ) is suggested below 75 K.